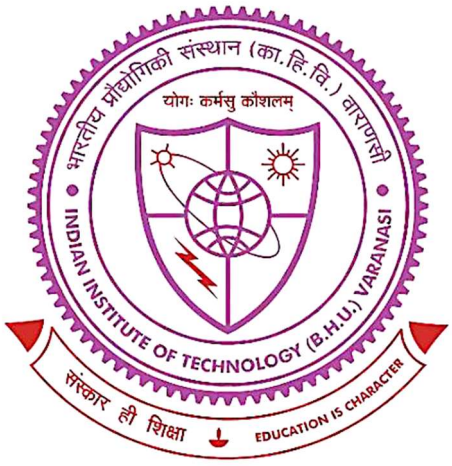
Microstructural evolution and phase stability in binary NiMn, semi-Heusler NiMnSb and NiMnSbV multicomponent alloy



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By

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Chapter 6 : Conclusions and Suggestions for Future Work

This chapter summarizes the major findings arising out of the present work. A detailed study on microstructural evolution and phase stability of equiatomic compositions of NiMn, semi-Heusler NiMnSb, V added semi-Heusler NiMnSbV induction melted concentrated alloys and equiatomic composition of mechanically alloyed medium-entropy alloys (MEAs) were carried out. Although the observation made on different aspects are listed at the end of the respective chapters, overall major findings are summarized as follows.

6.1 Conclusions

In the as-solidified equi-atomic NiMn alloy, along with the tetragonal η′ phase, a new monoclinic phase with P 2/m space group has been found. The lattice parameter of the mP8 phase is a=5.02 Å, b=5.16 Å, c=3.61 Å. The tetragonal η′ phase and the monoclinic phase form a self-assembled chessboard-like microstructure in the as-solidified alloy. In metallic systems, chessboard-like microstructure between a tetragonal and a monoclinic phase is being reported for the first time.

In the as-solidified NiMnSb alloy, cubic semi-Heusler NiMnSb phase and in the NiMnSbV alloy, cubic SbV_3 phase along with the semi-Heusler NiMnSb phase are observed. The SbV_3 phase nucleates and grows in the NiMnSbV alloy through solute rejection process. It is mildly faceted and lamellar structure is observed at the interface of SbV_3 with semi-Heusler NiMnSb phase. The SbV_3 phase is stable up to 700^{o}C, while the semi-Heusler NiMnSb phase is not stable beyond 400 ^{o}C and it transforms into hexagonal (Ni/Mn)Sb phase. The Cubic SbV_3 is a Frank-Kasper phase. In this phase, edge sharing 12-fold coordinated icosahedral clusters and 14-fold coordinated clusters are observed. The clusters are distorted, which might be a possible reason behind extensive formation of compound twins in this structure. Systematic substitution in the lattice of semi-Heusler NiMnSb alloy based on binary enthalpy of mixing and atomic radius mismatch may not be the ideal design strategy for the development of semi-Heusler NiMnSb based single phase multicomponent/high entropy alloys.

Ordered hexagonal (Ni/Mn)Sb phase forms upon mechanical alloying for 10 h in equi-atomic NiMnSb and NiMnSbV alloys, which is destabilized on further mechanical alloying to form a disordered hexagonal solid solution phase along with amorphous phase. Kinetics of formation of disordered hexagonal solid solution phase along with the amorphous phase from the ordered hexagonal (Ni/Mn)Sb phase is faster in NiMnSb alloy than the NiMnSbV alloy. NiMnSb semi-Heusler phase forms in the as-solidified NiMnSb alloy. In as-solidified NiMnSbV alloy, along with the NiMnSb semi-Heusler phase, Frank-Kasper type SbV_3 phase also forms through solute rejection mechanism. Phase formation in NiMnSb and NiMnSbV alloys is synthesis route dependent as the phases formed through mechanical alloying are different from the phases formed through solidification. Disordered hexagonal solid solution phase along with amorphous phase formation in NiMnSb and NiMnSbV alloys upon continued mechanical alloying may be attributed to the accumulation of strain in the lattice and increase in configurational entropy due to the presence of several elements. Systematic substitution in the lattice of semi-Heusler NiMnSb based on atomic radius mismatch and binary enthalpy of mixing is not the ideal way to design single-phase semi-Heusler based HEAs/MEAs.

6.2 Suggestions for future work

The nature of interface between two different crystallographic domains (tetragonal and monoclinic) in the as-solidified equi-atomic NiMn binary alloys can be studied through analytical TEM (phase contrast) and should be compared with the simulation. The precise orientation relationship between the phases is already known by the TEM, however EBSD (Electron Back Scattered Diffraction) can be done on the larger length scale to see the possibility of the presence of other 2-D defects. As the composition regime of this alloy system comes under the dotted regions in the phase diagram, the possibility of having more polymorphs related to the recently discovered monoclinic phase can be investigated.

The in-situ heating XRD experiments have already shown the evolution of (Ni/Mn)Sb phase in the semi-Heusler NiMnSb intermetallic with increasing temperature and the phase itself grows in terms of volume fraction w.r.t temperature, and it has also been shown that the (Ni/Mn)Sb phase nucleates at ~ 400 °C. The mechanism of

nucleation and growth and the nature of interface between (Ni/Mn)Sb and the matrix NiMnSb can be studied through in-situ heating in TEM.

The mechanically alloyed NiMnSb and NiMnSbV MEAs were studied and the evidence of amorphous phase formation can be seen in these alloys after long hours of high-energy ball milling. The extension of this work can be seen as the microstructural evolution and phase stability in SPS (spark plasma sintering) followed by mechanical alloying.